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(54) **Resin-calcium hydroxide composite restorative dental material**

(57) A restorative dental material for both lining deep cavities and providing temporary fillings includes calcium hydroxide, an organic resin binder, which can be polymerized by a redox reaction and which includes a bisphenol-A glycidyl methacrylate prepolymar, and a polymarization catalyst such as an organic peroxide and an amine. Also provided are compositions according to the invention in kit form which are ready for mixing by the dentist.

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SPECIFICATION

Resin composite calcium hydroxide restorative material

This invention relates generally to restorative dental materials and more particularly to a calcium hydroxide organic resin composite cavity liner.

In dealing with deep cavities, dentists usually line the bottom of a cavity with a layer of calcium hydroxide before filling the cavity with a permanent restorative material. Calcium hydroxide liners are known for their ability to stimulate the growth of secondary dentin and to neutralize the effects of acids and other chemicals.

Currently, liners of calcium hydroxide and the reaction products of 1,3-butylene glycol and methylsalicylate are widely used. By acid-base reaction, the reaction products of 1,3-butylene glycol-methylsalicylate react with the calcium hydroxide to form a set material. Two drawbacks of this system are its lack of strength when subjected to high condensing pressures, which can result in cracking of the liner when a filling is inserted, and its high solubility which limits its useful life.

A number of patents describe compositions which are useful as dental cements or cavity liners.

U.S. Patent 2,656,277 relates to an underfilling material which includes $Ca(OH)_2$, CaO, and casein which is mixed in water prior to application. U.S. Patent 3,047,408 relates to a composition which contains $Ca(OH)_2$ and a ester of salicylic acid and a polyhydric alcohol. U.S. Patent 3,367,788 relates to a cavity liner composition containing a calcium compound, preferably $Ca(OH)_2$, a radiopaque compound such as silver and an alkyl cellulose, preferably methyl cellulose, as a thickener. U.S. Patent 3,929,493 relates to a cavity liner which is prepared by mixing a calcium silicate and an organic acid such as tartaric acid, to form a calcium organic acid salt suspended in a network of silica. A dental base material which consists primarily of calcium hydroxide and which is reinforced by various materials such as polymethyl methacrylate to increase the compression strength to as high as 12,000 psi (82.7 MPa) is described as having a high pH which may damage the odontoblasts, thus impeding healing (col. 1 lines 61—68). U.S. Patent 4,064,619 relates to a cavity liner composition which includes a metal or alloy and an adhesive cement such as bis GMA which may be synthesized from the reaction of bisphenol A and glycidyl methacrylate (col. 4 lines 12—19).

Although filled organic resin binder materials are mechanically strong, they are biologically unkind to the dental pulp in that they can cause irritation and inflammation of the pulp.

The present invention is based on the discovery that dental cavity lining compositions and temporary fillings made from a calcium hydroxide and polymerizable organic resin binder which contains a bisphenol-A glycidyl methacrylate prepolymer and optionally an acrylic comonomer provide a strong, therapeutic cavity lining and temporary filling material. In particular, and surprisingly it has been found that when this organic resin binder is in combination with the calcium hydroxide, the irritation and inflammation which results from the use of the resin alone is greatly reduced or avoided.

In accordance with this invention, there is provided a dental restoration kit comprising calcium hydroxide, an organic binder material which can be polymerized by a redox reaction which includes a bisphenol-A glycidyl methacrylate prepolymer and a polymerization catalyst for the binder. Also provided is a cavity lining and temporary filling composition comprising a mixture of calcium hydroxide and the polymerized organic resin binder. The composition can also include other materials, such as glass and/or quartz fillers, pigments to match the tooth-color, and inhibitors to enhance the shelf life.

The compositions of the invention include calcium hydroxide powder with the finely powdered U.S.P or F.C.C. grade preferred. The calcium hydroxide is preferably used in amounts of from about 0.3 to 1 part by weight per part by weight of binder.

The organic binders in the compositions of the invention include resin systems which can be polymerized by a redox reaction. The binder systems which are preferred are based on materials which have been widely used in dentistry because of their easy handling and good mechanical properties. The system includes a bisphenol-A glycidyl methacrylate (BAGM) prepolymer with diluting acrylate monomers. Preferred monomers are difunctional methacrylates such as, for example, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and mixtures thereof.

The diluting monomers copolymerize and/or crosslink with the polymer to provide a set material having good adhesion to the tooth structure. The proportion of monomers to polymer can vary, depending upon the binder system over a range as is known to those skilled in the art. The amount should be sufficient to provide a workable mix but less than the amount which would impair the strength of the set system. Generally amounts of from about .05 to 3 parts by weight of monomer per part by weight of polymer can be used. The inclusion of small amounts (about .5 percent of weight of binder) of methacrylic acid in the bisphenol-A glycidyl methacrylate prepolymer system enhances the setting of the mixture to provide a quick hard set after the components of the kit are mixed and placed in the cavity.

The polymerization and crosslinking of the binder systems is initiated using an organic peroxide. Benzoyl peroxide (BPO) is used for this purpose in amounts which depend upon the

binder system and which generally range from about 0.1 to 3 percent by weight of the binder. An amine co-catalyst or accelerator is used, with the prepolymer system, to provide a redox catalyst system. Suitable amines for this purposa ara known in the art and include arometic amines such as, for example, N,N-dihydroxyethyl-p-toluidine (DHET) and dimethyl-p-toluidine (DMT) and mixtures thereof. Suitable amounts ranga from about 0.1 to 1 percent by weight of the binder.

Inhibitors or stabilizers are added to the monomer portion of the kits to provide longar shelf life particularly when the monomer portion includes an accelerator. Suitabla inhibitors include, for example, p-methoxyphenol (MEHQ) and 2,6-di-tert-butyl-4-methylphenol (BHT). Amounts of from about .02 to 0.2 percent by weight of bindar are used.

The compositions of the invention can also include filler matarials of, for exemple, gless, quartz end emorphoue fine silica. Tha fillar materials can be silane treeted to improva the resin to filler binding. The filler is used in amounts up to about 1.4 parts by weight per part by weight of binder with a preferred range of about 1 to 1.4. Suitable glasses are described, for example, in U.S. Patents 4,224,023 and 3,971,754 whose teachings are incorporated herein by reference. The gless compositions of U.S. Petent 4,224,023 ere silane treated and heve the following composition range by weight:—

1. 30—45 parts of quartz
2. 20—30 parts of aluminum oxide
3. 10—20 parts of cryolite
4. 4—10 parts of aluminum phosphate
5. 10—20 parts of fluorsper.

The gless compositions of U.S. Patent 3,971,754 include x-ray absorbing compounds such as strontium oxide and carbonate so that the boundaries of the filling are delineated on diagnostic x-rays.

Other ingredients which can be added to the compositions of tha invention include pigments, inert liquids and plasticizers. The pigments are added in trace amounts to metch the netural tooth color. Suitable pigments are oxides and sulfides of non-toxic metals such as yellow and red iron oxide (Fe_2O_3) and cadmium sulfide. Inert liquids such es N-ethyl-toluene sulfonamide are added in sufficient amounts to form pastes from dry ingredients. Suitable plasticizers for the compositions include, for exampla, metal steerates in amounts of about 0.1 to 0.3 percant by weight of the binder.

The ebove listed weight renges of the relative proportions of the materials in the final compositions ere approximate because the various ingredients of the compositions are divided into separate powder, liquid and/or paste components to form a kit. The components of the kit ere then mixed just prior to use in voluma rather than weight portions for the convenience of the user.

Exemples of three kits of the Invention are generally described below wherein parts ere parts by weight unless otherwise indicated.

Kit A (two powders and one liquid)

Powder A I	*Parts*
$Ca(OH)_2$	100
Fe_2O_3	trace (to make paste yellow)

Powder A II	*Parts*
Fillar (4 to 10 micron particle size)	100
Benzoyl Peroxide Catalyst (BPO)	0.2 to 2

where the filler can be one or any combination of
(1) quartz
(2) Glass as deecribed in U.S. 4,224,023
(3) Glass es deecribed in U.S. 3,971,754
(4) Amorphous fine silice (Ceb-o-sil, G. L. Cabot Inc.)

Liquid A	*Parts*
Bisphanol-A glycidyl methacrylate prepolymer (BAGM)	95 to 50
Monomars	5 to 50
Methacrylic Acid (MAA)	0.5
Amine acceleretor	0.1 to 1
inhibitor	0.02 to 0.2

wherein the monomers include any one or a combination of:—

(1) Ethylene glycol dimethacrylate (EGDMA)
(2) Triethylene glycol dimethacrylate
(3) Tatraethylene glycol dimethacrylate
(4) Hydroxyethyl methacrylate (HEMA)
(5) Hydroxypropyl methacrylate

where the amine accelerator is:—
N,N-dihydroxyethyl-p-toluidene (DHET) or dimethyl-p-toluidine (DMT) and mixtures thereof
where the inhibitor is:—
p-methoxyphenol (MEHQ) or 2,6-di-tert-butyl-4-methylphenol (BHT)

The composition is formed by mixing equal volumes of powders A I, A II and liquid A on a mixing pad. Optionally the pigmant can be included in either or both of A I or A II.

Kit B (3 pastes)

Pasta A	*Parts*
Filler (as in Kit A, Powder A II)	70 to 50
Prepolymer (BAGM)	23 to 36
Monomer (EGDMA)	7 to 14
Catalyst (BPO)	0.1 to 0.75
Inhibitor (MEHQ)	0.05 to 0.1

Paste B	*Parts*
Filler (as in Kit A, Powder A II)	70 to 50
Prepolymer (BAGM)	23 to 36

Monomers	7 to 14
Amine eccelerator (DHET)	0.1 to 1
Inhibitor (MEHQ)	0.05 to 0.1
Fe_2O_3 (red)	trace (to make paste slightly rad)

where the monomers include HEMA or EGOMA or e mixture of both.

Paste C	*Parts*
$Ca(OH)_2$ powder	40 to 60
Zinc Steerate plasticizer	0.1 to 0.3
N-ethyl-toluene sulfonemide inert liquid	60 to 40
Fe_2O_3 (yellow)	trace (to make paste yellow)

The composition is formed by mixing equel volumes of each peste.

Kit C 2 liquids end 1 paste

Liquid A	*Parts*
Prepolymer (BAGM)	23 to 36
Monomer (EGOMA)	7 to 14
Cetelyst (BPO)	0.1 to 0.75
Inhibitor (MEHQ)	0.05 to 0.1

Liquid B	*Parts*
Prepolymer (BAGM)	23 to 36
Monomere	7 to 14
Amine eccalerator (DHET)	0.1 to 1
Inhibitor (MEHQ)	0.05 to 0.1
Fe_2O_3 (red)	trace (to make paste slightly red)

where the monomers include HEMA or EGDMA or e mixture of both.

Paste C	*Parts*
$Ca(OH)_2$ powder	40 to 60
Zinc Stearate plesticizer	0.1 to 0.3
N-ethyl-toluene sulfonemide inert liquid;	60 to 40
Fe_2O_3 (yellow)	trace (to maka paste slightly yellow)

The composition is found by mixing equal volumes of the two liquids and peste.

Example 1

A clinical evaluation was performed using a kit according to Kit A having the following component compositions:—

Powder A I	*Parts*
$Ce(OH)_2$ powder F.C.C. grade by Beker Chemicals Co.	100
Powder A II	*Parts*
Silane treated glass of U.S. Patent 4,224,023	100
BPO containing 20% water	1.3
Fine silica	0.1
Fe_2O_3 yellow pigment	0.02

Liquid B	*Parts*
BAGM	56
HEMA	15
EGDMA	28
MAA	0.5
MEHQ	0.08
DHET	0.5

The composite mixture is formed by mixing equal volumes of Powdar A I and A II with 5 drops of Liquid A using an eyedropper.

Properties:

Working time — ebout 2 minutes

Compressive strength *—15,000 to 20,000 psi

Ph of water immersing e specimen 11 — after 5 minutes

The test method used is aimilar to ADA specification ≠B,4.3.4 except thet the mixture hes to be placed into the mold within $1\frac{1}{2}$ minutes after commencing tha mixing.

A clinicel evaluation was made on monkays with good pulp response et 3, 21 end 60 days after plecement in deep cevities. Reparetive dentin wes observed 60 deys after plecement.

Example 2

As a comparison, the typical composition and properties of a conventionel calcium hydroxida cavity liner are as follows:—

Calcium hydroxide paste	*Perts*
$Ca(OH)_2$ U.S.P	2
N-ethyl-toluene sulfonamida	1
Zinc oxide	0.5

Selicylate peste	*Parts*
Titanium dioxide	1
1,3-Butenediol-methyl salicylate reaction product (U.S. 3,047,408)	1

Equal volumes of the two pastes are mixed.

Properties:

Working time	3 to 4 minutes
Compressive strength	1,000 to 2,000 psi
pH in watar	12 in 5 minutes

Clinical: similar to Example 1.

The evaluations of the composite meterial of Example 1 demonstrete thet the compoeitions of the invantion possess the tharapeutic properties of calcium hydroxide liners and the strength of resins without tha inflammation usually associated with filled resins. The strength properties also provide the ability to use the compositions as temporery filling matarieis. The compressive strength, in comparison to the conventional calcium hydroxide liner of Example 2, enhances the ability of the liner to protect the tooth structure becausa it it less subject to cracking and leakaga of harmful materials into the tooth beneath the filling.

Claims

1. A dental restorative kit or composition for lining or temporarily filling dental cavities which comprises calcium hydroxide and a polymerizable organic binder, wherein the binder comprises a bisphenol-A glycidyl methacrylate prepolymer.

2. A kit or composition according to claim 1, containing from 0.3 to 1 part by weight of calcium hydroxide per part by weight of the organic binder.

3. A kit or composition according to claim 1 or 2, wherein the binder comprises a mixture of a bisphenol-A glycidyl methacrylate prepolymer and an acrylic comonomer.

4. A kit or composition according to claim 3, wherein the binder contains from 0.05 to 3 parts by weight of acrylic comonomer per part by weight of prepolymer.

5. A kit or composition according to claim 3 or 4, wherein the comonomer is a difunctional methacrylate.

6. A kit or composition according to claim 5, in which the binder additionally contains up to 0.5% by weight of methacrylic acid.

7. A kit or composition according to any one of claims 1—6, which additionally contains a filler.

8. A kit or composition according to claim 7, wherein the filler comprises glass, quartz or amorphous silica.

9. A kit or composition according to claim 7 or 8, wherein the filler is present in an amount of from 1 to 1.4 parts by weight per part by weight of the binder.

10. A kit according to any one of claim 1—8, wherein additionally contains a catalyst for the polymerization of said binder.

11. A kit according to claim 10, wherein the catalyst in an organic peroxide.

12. A kit according to claim 11, wherein the peroxide is banzoyl paroxide.

13. A kit according to any one of claims 7—12, in which at laast one of the componants of the kit comprises an amine polymerization accelerator.

14. A kit according to any one of claims 10—13, in which the binder component comprises a polymerization inhibitor.

15. A kit according to eny one of claims 10—14, which contains three separate components ready for admixture to form the lining or temporary filling material, the three separete components comprising, respectively

A. calcium hydroxide

B. the binder

C. the catalyst

16. A kit according to claim 15, as dependent upon claim 7, 8 or 9, wherein the filler is contained in component B and/or C.

17. A kit according to claim 15 or 16, as dependant upon claim 14, wherein component C contains a proportion of the bisphenol-A glycidyl methacrylate prepolymer and/or the acrylic comonomer, if present, plus at least a proportion of the catalyst and at least a proportion of the polymerization inhibitor.

18. A dental cavity lining or tamporary filling material compriaing a composition as claimed in any one of claims 1—9 in which the calcium hydroxide, the binder and the filler, if present, are in an admixture, and in which the binder has been cured by *in situ* polymerization of the bisphenol-A glycidyl methacrylate and acrylic comonomer, if present, initiated by a redox polymerization catalyst.

19. A material according to claim 18, wherein the binder is cured by polymerization initiated by a redox polymerization catalyst comprising an organic peroxide and an amine polymerization accelerator.

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